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PROCEEDINGS

An Innovative Method For Rapid Detection of Microbiologically Influenced Corrosion

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INTRODUCTION

Microbiologically influenced corrosion (MIC), the interaction of biological activity with corrosion processes, is a significant cause of degradation of piping and heat transfer surfaces in cooling water systems. MIC can produce localized corrosion and through-wall penetration of piping and heat exchanger tubing at rates 10 to 1000 times more rapid than those normally encountered.

Monitoring of biofilm formation on line provides the system operator with the information needed to initiate mitigation activities, such as cleaning and water treatment, well before the structural integrity of piping or components is jeopardized. On-line monitoring of biofilms, and timely actions, taken before corrosion has initiated or thick biofilms are formed on piping or heat exchanger tube surfaces, can significantly improve the effectiveness of mitigation activities. Continuous monitoring of biofilm activity permits close control of biocide additions (to avoid over-treatment of the water) and scheduling of **preventive** maintenance activities so that unplanned downtime due to MIC is avoided.

The electrochemical aspects of MIC have been discussed by a number of authors [1-8]. Since MIC affects electrochemical reactions that influence corrosion, biofilm activity may be tracked by electrochemical monitoring methods that are specific to those electrochemical reactions by which biofilms can influence corrosion. An electrochemical device, the BIoGEORGE™ probe, has been developed[1] to provide a method for determining the onset of biofilm formation on metal surfaces and tracking biofilm activity on line in a power plant or industrial environment [9].

BACKGROUND

The BIoGEORGE probe (Figure 1) consists of two sets of identical metallic disks, separated from each other by an insulating epoxy. The cylindrical probe is inserted into the plant environment via a standard access fitting, such as a threaded tee. A simple control system cathodically polarizes one electrode (i.e., set of disks) relative to the other for a short period (30 minutes to one hour) each day. The electrodes are connected through a precision resistor (e.g., 1000 Ω) at all other times. By monitoring the current required to achieve the pre-set potential over a period of days or weeks, the influence of biofilms on operative half-reactions may be readily detected. The "gentle" cathodic polarization simulates electrochemical conditions similar to those resulting from local anodic sites (e.g., inclusions or weldments) and produces local environments that result in differences in the types and numbers of microorganisms present on each electrode [3, 10-11].

The **applied current**, the current which flows when the external power source is on, is tracked daily. When a biofilm becomes established on the probe surfaces, this applied current exhibits a distinct increase. Examination of the trend of applied current thus provides rapid, real time indication of biological activity on the probe surfaces. The **generated current**, the current that flows through the shunt resistor which connects the electrodes when the power source is off, is monitored at all otherr times. Initially, the generated current is zero or very near zero as would be expected for two nominally identical electrodes exposed to the same environment. Laboratory tests have shown that the generated current also

[1] Patent rights to the BIoGEORGE probe are owned by the Electric Power Research Institute. The patent application was filed in October, 1991. U.S. Patent Number 5,246,560 was issued on September 21, 1993.

increases when a biofilm forms. Biofilm formation is monitored by tracking both parameters.

APPROACH

Probes were tested in seawater environments typical of those encountered in piping and heat exchangers of Naval vessels. Probes were assembled using electrodes with materials with different film-forming characteristics. The influences of material type and the polarization schedule (i.e., length of time that electrodes are polarized and the pre-set potential) on the sensor's ability to indicate the formation of biofilm and the onset of MIC were evaluated. These probes were then installed into natural and synthetic seawater systems and tested over periods of six to eight weeks. The applied and generated currents were monitored.

Copper alloys and titanium are commonly used in seawater systems because of their superior resistance to pitting in chloride-containing environments. Standard design probes, with Type 304L stainless steel electrodes, and probes with 90-10 copper-nickel, and titanium (Grade 2) electrodes were exposed in both static laboratory tests and in a slowly flowing seawater flume at the Naval Surface Warfare Center's Corrosion Test Facility (Ft. Lauderdale, FL).

The on-line measurements were supplemented by post-exposure testing to characterize the microbiology, local chemistry (including corrosion deposits and areas away from the local corrosion site), and corrosion of surfaces.

Static Seawater Tests

Probes were exposed to a synthetic seawater environment (ASTM D-1141) in a 10 liter plexiglass vessel that was covered with aluminum foil to keep out light. Communication with room air was permitted. Deionized water was added as needed to keep the level well above the probe electrodes.

Data acquisition was accomplished using a single two-channel Allen recorder and a series of timers and switches that produced a trace for each probe two times a day. The results were input to QuattroPro, Version 5.0, for analysis and plotting.

The stainless steel electrodes were polarized to 100 mV, the 90-10 copper-nickel to 50 mV, and the titanium electrodes to 400 mV. These values were selected to provide readily measurable currents, hopefully, without corroding the electrodes excessively.

After permitting the cells to stabilize for three days, a mud was slowly added to the system (volume of mud = 4% of total electrolyte volume) to introduce organic activity. The mud was produced by mixing a soil taken from Pacific Gas & Electric's Pittsburg (California) Power Plant site and mixing it with artificial seawater in a 1:1 volume ratio. A number of components from the power plant had experienced MIC attack, generally the result of SRB, in this soil.

After approximately 50 days of exposure, a 5.25% sodium hypochlorite solution was added to the electrolyte to produce a concentration of approximately 8 ppm free chlorine. Probe response was then monitored for an additional eleven days. Nine days later, free chlorine concentration was measured at 1 ppm. At the end of the test, no free chlorine was detected.

Electrodes were monitored for microbiological activity 47 days after inoculation in the second test using MICKits (Bioindustrial Technologies, Incorporated, Georgetown, TX). Local pH on the probe electrodes was determined (Horiba Compact pH Meter, Model Cardy C-1) 47 days into the test and at the completion of the testing. The pH of the environment was tested at the beginning and the end of the test. Chlorine was measured using an Olin, HTH test kit.

Flowing Seawater Tests

Probes were also exposed to flowing natural marine environments at the Naval Surface Warfare Center at a continuous, slow flow to optimize microbiological colonization (transport of nutrients, etc.) without stripping biofilms from the metal surfaces. Like the static exposures, these tests were run such that the probe and test environment were always completely dark, as would be the case for shipboard heat exchange systems.

The BIoGEORGE™ probe electrodes at NSWC were initially polarized to 200 mV (relative to each other) for 30 minutes per day using the standard probe control system. Data were recorded using a Chessell Model 4200 recorder interfaced to an XT-class computer. Data trends were plotted in QuattroPro, Version 5.0.

After 79 days of exposure, the probes were removed from the flume, photographed, and the surfaces characterized. Field microbiological analysis was performed on samples from the positive and negative polarity electrodes from each probe using MICKits. The probes were then cleaned and returned to service.

For the second flowing test, the polarization potential was increased for the titanium probe (from 200 to 400 mV) and decreased for the stainless steel (from 200 to 60 mV) and 90-10 copper-nickel (200 to 25 mV). The polarization time for all probes was increased to one hour.

RESULTS

Static Seawater Tests

Figure 2 summarizes the results from the static tests. The applied and generated currents for the stainless steel probe remained stable following the inoculation of the cell, but both currents changed rapidly ten days later. Interestingly, the generated current shifted in the negative direction several days after the inoculation and was of a sufficient magnitude so that the applied current was also negative. The **difference** between the applied current and generated current provided the most useful parameter for plotting. The addition of sodium hypochlorite caused the current difference to return to near its original value.

The applied and generated currents from the titanium probe were much smaller, however, the response characteristic was very similar to that of the stainless steel probe. The applied current exhibited a distinct increase eleven days after inoculation. The generated current was essentially zero initially, but exhibited a very definite increase fourteen days after inoculation. The response of the probe to the destruction of the biofilm by hypochlorite is also readily apparent.

Both the stainless steel and titanium electrodes exhibited an increased concentration of general aerobic bacteria, general anaerobic bacteria, acid producers, and SRB when compared to the bulk fluid. Following biocide addition, the enrichment of SRB was no longer observed. The 90-10 copper-nickel electrodes exhibited low concentrations of all the detectable microbes, consistent with the lack of response from the probe.

Flowing Seawater Tests

In the first month of exposure, the applied and generated current traces from the stainless steel probe were very similar to those from the static tests. Applied currents stabilized after a few days, then both applied and generated currents increased steadily for the next three days. The applied current reached a maximum of ~100 μA and the generated current increased from -20 μA to nearly 33 μA, both currents remained at those levels until a problem with the system pump caused an eighteen day interruption to system flow. During the time that the flow was interrupted, applied current decreased and became more unstable while the generated current decreased to near zero. When the pump was restarted, the applied current quickly returned to a value near 100 μA. The generated current responded more slowly but reached a value of about 10 μA that persisted through the end of the test. The generated current appeared to provide the more sensitive indicator of biofilm activity (Figure 3).

The titanium probe exhibited very small applied currents (of the order of 1 μA) and even smaller generated currents (-0.4 μA) as shown in Figure 4. The applied current remained very steady, until the eighteen day stagnant period. About ten days after the flow stopped, the applied current increased rapidly to a value in excess of 5 μA, then gradually decreased to a steady value slightly higher than that which had been observed prior to the abrupt increase. Once the pump was restarted, the new, higher value persisted for 21 days. When the generated currents were plotted on an expanded scale, a very definite positive shift in generated current was observed five days after the start of the test, in exact agreement with changes in the generated current on stainless steel. While the pump was off, the generated current was much less stable. Once the pump was returned to service, the generated current again exhibited a positive shift.

As in the static tests, the 90-10 copper nickel probe gave no indication of biofilm formation. Post-test examination of the probes revealed minimal deposition on the 90-10 and titanium probes, and heavy, rust colored deposits on the stainless steel probe. The stainless steel probe exhibited some macrofouling and very heavy deposition of corrosion products on the probe body. Rusty deposits were observed on the electrodes, especially the disks near the bottom of the probe. All of the 90-10 copper-nickel electrodes were a fairly uniform, greenish-tan color. Small copper or rust colored spots were obvious on all of the 90-10 electrodes. The titanium electrodes were a uniform matte gray color with little or no evidence of deposits.

Microbiological and chemical samples were collected from the three disks of each polarity nearest the end of the probe (i.e., the most deeply submersed disks) on sterile cotton swabs. Serial dilutions were then performed in accordance with the kit instructions and detailed microbiological analysis (by microscopy) and chemical analysis for pH, chloride, iron, manganese, and calcium were performed by BTI. A summary of the results is given in Table 1.

The microbiological results confirmed the presence of biofilms on the stainless steel and titanium electrodes. Comparing the relative proportions of sulfate reducing bacteria, acid producing bacteria, and general aerobic and general anaerobic populations on the different electrodes and the bulk water revealed that the negative electrodes of the stainless steel and titanium probe supported a biofilm of the same approximate composition as that of the bulk water. Far fewer acid producers were detected on the positive electrodes of each of those probes. Iron depositing bacteria were only detected (microscopically) on the stainless steel electrodes and in the deposit from the probe body. Almost no viable microorganisms were detected on the 90-10 copper-nickel probe electrodes; consistent with the absence of any increases in applied current or generated currents from the probe.

The deposits were removed and the probes returned to service for Test #2. The cleaning process was very simple. The copper-nickel and titanium probes were cleaned completely by a fresh water rinse only. Considerable deposit remained on the stainless steel electrodes even after wiping the probe with a wet paper towel. The deposit was removed by popping it loose with a fingernail. Removal of the deposits revealed bright and shiny electrodes with no evidence of corrosion damage.

In the second test at the NSWC Corrosion Test Site, the polarization parameters were modified to decrease corrosion damage on the stainless steel and 90-10 copper-nickel probes and to produce values of applied currents on the titanium probe that were more readily measured.

The stainless steel probe responded in a very similar fashion as in Test #1 except that the magnitude of the applied current was less than that for Test #1 where the applied potential was higher. Both applied and generated currents appeared to be sensitive to flow, as before. Once again, the applied current decreased and generated current became less stable when the flow was interrupted. Generated current again provided a

more sensitive indicator - currents increased from essentially zero to near 20 μA a week or so after the start of the exposure.

The applied and generated currents on the 90-10 copper-nickel probe were smaller than had been observed in the first test, however, the probe still did not appear to provide any useful information on biofilm activity on surfaces, probably because little or no biofilm was grown on the electrodes.

The larger applied potential between the titanium electrodes provided very stable outputs and readily measurable applied and generated currents. The applied current was stable at a value of about 2 μA for most of the exposure. As noted in the first test, the magnitude of the currents increased and became less stable when the flow was stopped. The generated current remained at essentially zero for the first week of exposure, then increased rapidly to about 0.25 μA.

CONCLUSIONS

- The BIOGEORGE™ probe provides a practical method for the detection of biofilms, on-line, in a seawater system.
- Probes fabricated using either stainless steel or titanium electrodes provide positive indications of biofilm formation, and the destruction of the biofilm from the application of biocide.
- Probes using 90-10 copper-nickel were not as successful in static seawater, inoculated with a high SRB mud, or in a flowing, natural seawater environment.
- Indications of biofilm activity were confirmed by post-test examination.
- Additional refinements of the hardware and method are recommended.

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Mr. Scott Hoover and Mr. John Braker of the NSWC Corrosion Test provided valuable assistance with installation and data acquisition.

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Table 1

Chemical and Microbiological Characterization of Electrodes - NSWC Test #1

(Microbial counts as cells/cm^2)

Sample	SRB	APB	General Aerobic	General Anaerobic	Iron Depositing Bacteria[1]
SS+	≤ 1	~1	$\sim 10^2$	$\sim 10^2$	+
SS-	≤ 1	$\sim 10^4$	~10	~10	+
90-10+	ND	ND	≤ 1	ND	-
90-10-	ND	~1	ND	~1	-
Ti+	≤ 1	~10	~10	$\sim 10^2$	-
Ti-	≤ 1	$\sim 10^3$	~10	$\sim 10^2$	-
PLUG[2]	ND	ND	ND	ND	+
Microbial Counts as cells/cc					
Bulk Water	$1 \rightarrow 10$	$10^3 \rightarrow 10^4$	$10 \rightarrow 100$	$10^2 \rightarrow 10^3$	-

			Chemical Analysis, ppm (except for pH)							
Sample	pH	Fe	Mn	Cr	Ni	Mg	Ca	Cu	Ti	Cl
SS+	8.1	<1.5	0.75	<2.5	<2.0	NA	38	NA	NA	2100
SS-	8.0	<0.75	<0.25	<1.3	<1.0	NA	18	NA	NA	1400
90-10+	8.1	3.6	<0.25	NA	2.4	NA	9.1	9.7	NA	530
90-10-	6.3	<0.75	<0.25	NA	<1.0	NA	3.1	0.63	NA	960
Ti+	7.6	<0.75	<0.25	NA	NA	NA	5.6	NA	<10	2500
Ti-	8.0	<0.75	<0.25	NA	NA	NA	7.9	NA	<10	1900
Bulk water	8.0	NA	0.38	NA	NA	1300	440	NA	NA	19200

[1]From direct microscopic examination by BTI

[2]Corrosion deposit from stainless steel body of titanium probe

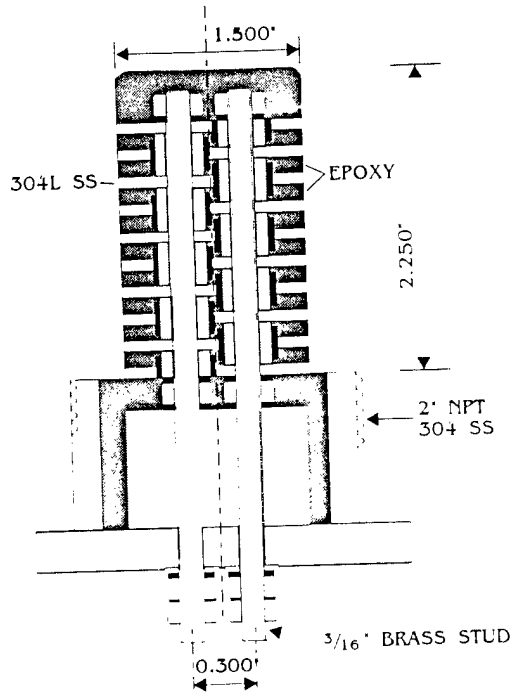

Figure 1. BIOGEORGE Electrochemical Biofilm Probe

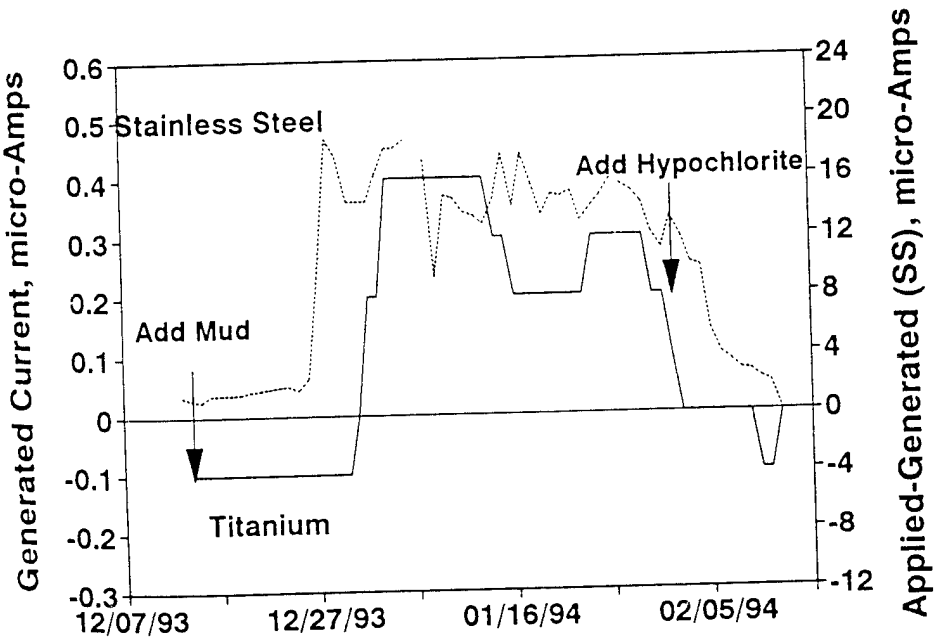

Figure 2. Results from Static Seawater Test
(Titanium at 400mV; Stainless Steel at 100mV)

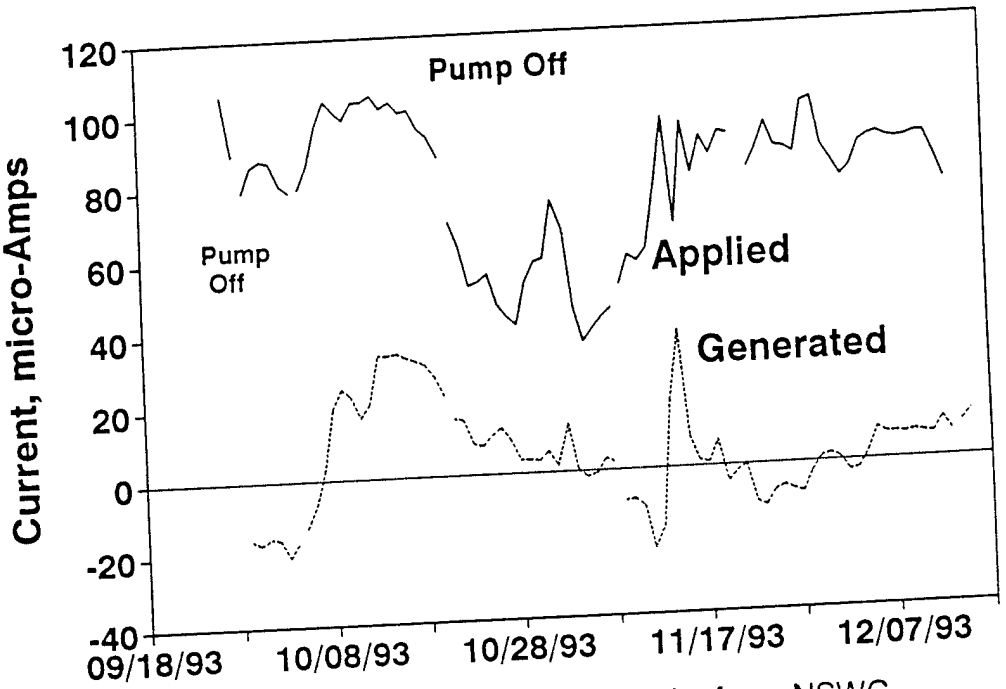

Figure 3. BIoGEORGE Probe Results from NSWC (Stainless Steel, 200 mV, Test #1)

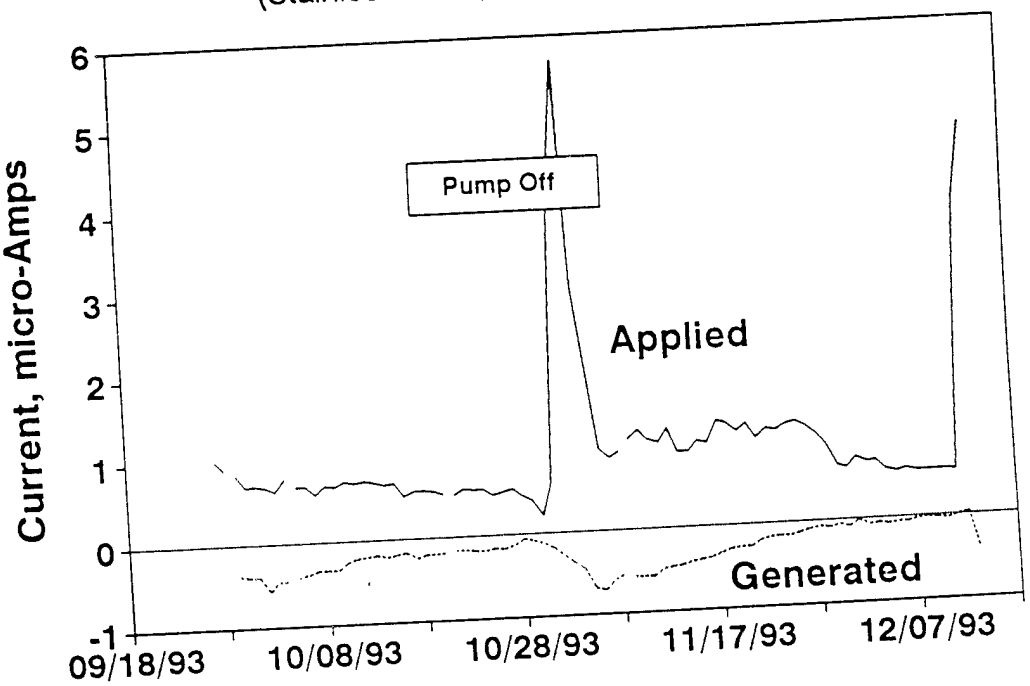

Figure 4. BIoGEORGE Probes Results from NSWC (Titanium, 200mV, Test #1)